

LASER SURFACE INTERACTION OF HIGH- $T_c$  SUPERCONDUCTORS

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## ABSTRACT

During the past two years, one of the most exciting research fields in science has been the study of the newly discovered high- $T_c$  metal oxide superconductors. Although many theoretical models were proposed, there has been no general agreement on any theory to explain these materials. One of the "peculiar" features of these high- $T_c$  materials is the noninteger number of oxygen atoms. The oxygen content is extremely critical to the superconductive properties. Our results from mass spectroscopy of laser desorbed species indicate that significant quantities of oxygen molecules are trapped in the bulk of these superconductors. It appears that these trapped oxygen molecules may play key roles in superconductive properties.

## INTRODUCTION

In 1986, Bendorz and Muller<sup>1</sup> discovered that metallic oxide with a perovskite structure in the La-Ba-Cu-O system exhibited superconductivity at 20°K. In early 1987, Chu and his co-workers<sup>2</sup> made a  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound which had a  $T_c$  higher than the temperature of liquid nitrogen. Since these discoveries, the research and development of high- $T_c$  superconductors has aroused unprecedented attention, not only from the scientific community, but also from various industries and governments. As these new superconducting materials are in general very "brittle" and difficult to machine, it is extremely difficult to fabricate them into thin wires. In addition, practical use of new high- $T_c$  superconductors will require materials with very high critical current density. Thus thin film preparation is particularly important for many applications of superconductors, such as electronics for the computer industry. Films with high superconducting transition temperatures have been prepared by electron beam evaporation, organometallic chemical vapor deposition, DC sputtering, molecular beam epitaxy, and laser evaporation and deposition processes. For example, Rice *et al.*<sup>3</sup> used electron beam and thermal evaporation to produce Ca-Sr-Bi-Cu-O superconducting films from  $\text{CaF}_2$ ,  $\text{SrF}_2$ , Bi, and Cu targets. Berry *et al.*<sup>4</sup> produced a superconductive film by organometallic chemical vapor deposition. Hellman *et al.*<sup>5</sup> used molecular beam epitaxy to produce a  $\text{DyBa}_2\text{Cu}_3\text{O}_{7-x}$  film on a  $\text{SrTiO}_3$  substrate. Lynds *et al.*<sup>6</sup> used a Nd-YAG laser beam to do laser evaporation and deposition to prepare a  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  thin film from targets of  $\text{Y}_2\text{O}_3$ ,  $\text{Ba}_2\text{CO}_3$ , and CuO. Kwok *et al.*<sup>7</sup> applied a homogeneous excimer laser to obtain a film with the right stoichiometry of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . However, most of the films in the works cited above need to be annealed in an oxygen environment in order to produce superconductivity. Recently, several research groups obtained superconductive films of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  by raising the temperature of the substrate and introducing oxygen into the chamber during the thin film preparation process.<sup>8</sup> However, no superconductive films of the Bi-Sr-Ca-Cu-O or Tl-Sr-Ba-Cu-O systems were obtained without oxygen annealing. Nevertheless, the right ratio of various metal elements is one of the key factors in achieving superconductivity. Superconductive films are usually obtained based on repeated trials and adjustments. Venkatesan *et al.*<sup>9</sup> observed two distinct components during pulsed laser deposition of high- $T_c$  superconductive film. It was pointed out that the quality of the

superconductive film depends on controlling the film stoichiometry. The role of introducing oxygen into the thin film preparation chamber has never been fully understood. Thus, the need for a real-time monitor for high- $T_c$  thin film preparation is quite critical.

In general, the preparation of a superconductive thin film involves the vaporization of various chemicals. The species deposited on substrates include neutral atoms or molecules in ground states, atoms and molecules in excited states, ions in ground states and ions in excited states. An instrument which has the capability of the quantitative determination of atoms, molecules, and ions in various electronic states should provide very detailed information on the mechanism of formation of superconductive films. A position sensitive monitor of various oxide compounds relative to the flow and pressure of oxygen should reveal the role of oxygen in superconductive film preparation. An ideal method of monitoring the deposition process is to continuously track the deposition *in situ* and automatically maintain optimum film growth. With this goal in mind, we have investigated several diagnostic methods. In this work, fluorescence spectra are presented which indicate suitability for monitoring excited atoms, molecules, and ions; mass analysis of laser desorbed ions is described; and the application of resonance ionization spectroscopy (RIS) to monitor desorbed neutral atoms and molecules is discussed.

One of the "peculiar" features of these high- $T_c$  materials is the noninteger number of oxygen atoms. The oxygen content is extremely critical to the superconductive properties. All of the bulk metal oxide superconductors need to be annealed in an oxygen environment for an extensive period of time in order to achieve superconductivity. The oxygen content is equally critical to bulk and thin film superconductors. Take  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  as an example. Its superconductive properties disappear whenever  $x$  is larger than 0.5. The samples not only need to be sintered in the oxygen environment, but also need to be cooled down slowly to take up oxygen.<sup>10</sup>

Batlogg *et al.*<sup>11</sup> and Leary *et al.*<sup>12</sup> observed a very small isotopic effect by replacing  $^{16}\text{O}$  with  $^{18}\text{O}$  for the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  system and concluded that weak electron-phonon coupling cannot be used to explain this observation. The crystal structures of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  have been studied very extensively by X-ray diffraction and neutron diffraction.<sup>13</sup> It was confirmed as orthorhombic for  $x = 0$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . However, the crystal structure becomes tetragonal when  $x \geq 0.5$ . It was widely speculated that the change in crystal structure was responsible for the loss of superconductivity. However, experimental results by Xiao *et al.*<sup>14</sup> indicate that the crystal structure is not the key for superconductivity. It was pointed out that the  $T_c$  of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  is determined mostly by the actual oxygen content rather than its configuration and that the oxygen-vacancy order was found to be insignificant for high- $T_c$  superconductors. From the viewpoint of valence numbers for the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound, the number of oxygen atoms should be 6.5 (i.e.,  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ ). Unfortunately, it has been proven experimentally that a single crystal of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  does not demonstrate superconductivity. The number of O atoms needs to be higher than 6.5 for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  to achieve superconductivity. A similar situation is true for all other high- $T_c$  metal oxide superconductors. Thus the existence of  $\text{Cu}^{+3}$  in these high- $T_c$  superconductors was suggested in order to account for the chemical structure. However, Sarma and Rao<sup>15</sup>, as well as Horn *et al.*<sup>16</sup> used X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) to investigate the chemical state of the copper ion. They found that  $\text{Cu}^{+3}$  was not present in these superconductors. Instead,  $\text{Cu}^+$  was observed. It is well known that high- $T_c$  superconductors in an oxygen-free atmosphere will lose oxygen. It has been assumed that the oxide anion ( $\text{O}^{2-}$ ) in the  $\text{CuO}$  plane is in equilibrium with oxygen molecules in the gas phase at the same temperature and a fixed partial pressure. It is known that these metal oxide superconductors are, in general, very porous and that there are many

deficit sites in the crystal. However, the possible existence of trapped  $O_2$  molecules in the bulk or thin film materials has been ignored. During the development of the present monitor for superconductive films preparation, we observed the existence of trapped  $O_2$  in superconductors.<sup>17</sup> The trapped  $O_2$  gas can possibly have significant implications for the nature of the superconductivity of these high- $T_c$  materials.

## EXPERIMENTAL RESULTS AND DISCUSSION

A schematic of the experimental apparatus is shown in Fig. 1. A Nd:YAG laser beam was used to do laser ablation of samples. A quadrupole mass spectrometer was used to monitor the desorbed ions directly. The desorbed neutral atoms or molecules were ionized by electron impact or by a laser resonance ionization method. Fluorescence spectra were obtained from excited atoms and molecules.<sup>18</sup> Different samples of superconductors were used in this work. One was produced from an aqueous solution containing Y, Ba, and Cu salts and oxalic acid via a homogeneous coprecipitation technique using urea. Others were made by a standard solid-state chemistry approach. Transition temperatures of samples for Y - Ba - Cu - O and Bi - Sr - Ca - Cu - O were measured as  $\sim 92^\circ\text{K}$  and  $\sim 125^\circ\text{K}$ , respectively. Most fluorescence data were taken using laser ablation of the superconductor sample by the fundamental of a Nd:YAG laser beam. Most secondary ion spectra were obtained using the second harmonic of the Nd:YAG laser beam. However, the data obtained with different harmonics show very little dependence on the frequency of the laser beam. The laser beam power density on the superconductor target was varied from  $5 \times 10^5 \text{ W/cm}^2$  to  $1 \times 10^9 \text{ W/cm}^2$ . In general, breakdown occurs when the laser power density is higher than  $1 \times 10^7 \text{ W/cm}^2$ . Insufficient photons could be detected to monitor fluorescence in the absence of laser-induced breakdown. However, the fluorescence spectra remain constant as long as laser-induced breakdown occurs. The laser energy per pulse was measured by a Scientech calorimeter. The laser beam pulse duration was 5-7 ns which was measured by a fast response photodiode. A Pellin-Broca prism was used to separate different harmonics of the laser beams. Since this laser utilized an unstable resonator, the typical laser beam distribution was a doughnut shape. Fluorescence spectra were obtained by using a GCA McPherson spectrometer which can be scanned automatically. The resolution of the monochromator was fixed at  $4 \text{ cm}^{-1}$ . A photomultiplier (RCA 31034) which has an almost flat response for visible and near-infrared (IR) photons was used to detect the wavelength-resolved photons. Since the laser beam was pulsed, the fluorescent light detected by the photomultiplier was gated for  $20 \mu\text{s}$  so that the background from room light or dark current of the phototube could be neglected. The output of the phototube went through a charge-sensitive preamplifier followed by a pulse-shaping amplifier. It then went to a sample and hold circuit which drove a recorder.

The entire fluorescence spectra in the visible and near-IR region for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and  $\text{Tl-Ba-Ca-Cu-O}$  are shown in Fig. 2 and Fig. 3. The fluorescence spectra of  $\text{CuO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{CaO}$ , and  $\text{BaCO}_3$  were also obtained as an aid in the identification of the peaks in the fluorescence spectra of these two superconductors. The emission due to different metal elements was identified from atomic spectra. Many different transitions for Y, Ba, and Ca were observed. However, no definite indication of transitions due to copper atoms, which had been suggested as the key element for superconductive properties, was observed. No clear spectra corresponding to  $\text{CuO}$  transitions were identified. The complete fluorescence spectra of high- $T_c$  superconductors are quite complicated. However, the sharp transition lines, especially in the red and near-IR spectral regions, should be convenient for use in monitoring the concentration of most metal elements, since the broad continuum emission due to the plasma can be neglected in this region. The fluorescence band for YO was also observed in the Y-Ba-Cu-O system. Absolute fluorescence quantum yields can be obtained

by using the fluorescence of a dye solution excited by the frequency doubled Nd:YAG laser beam.<sup>19</sup>

Elements which provide low emission intensity such as Cu and Tl can be monitored by desorbed ion spectra. Ion spectra of laser-ablated Y-Ba-Cu-O and Tl-Ca-Ba-Cu-O are shown in Fig. 4(b) and Fig. 4(c) with a laser power density of  $2 \times 10^7$  W/cm<sup>2</sup>. YO<sup>+</sup> signals were observed to be much stronger than the signal of BaO<sup>+</sup> for the Y-Ba-Cu-O system for a modest ablation laser energy. No CuO<sup>+</sup> signals were observed for the Y-Ba-Cu-O or Tl-Ca-Ba-Cu-O systems. The crystal structure of Y-Ba-Cu-O has been extensively studied by X-ray diffraction and neutron scattering methods.<sup>20</sup> There were no oxide atoms on the Y plane. Thus the formation of YO<sup>+</sup> was thought to be either from peroxide or from trapped oxygen molecules. For the Tl-Ca-Ba-Cu-O system, CaO<sup>+</sup> was observed, although X-ray diffraction data indicate that there are no oxides on the Ca plane. The formation of YO<sup>+</sup> and CaO<sup>+</sup> can possibly come from the chemical reaction between Ca or Y atoms with oxygen in the plume just above the surface. Secondary ion spectra obtained in this work are much simpler than the results from atom probe experiments.

The major species detected following laser ablation of superconductors are neutral atoms and molecules in the ground state. However, it is difficult to detect most of these desorbed species by a conventional mass spectrometer with an electron impact ionizer due to the low density of the desorbed neutral molecules. However, RIS has been demonstrated to have the capability of detecting a single neutral metal atom.<sup>21</sup> Recently, the detection of Bi atoms from the Bi-Sr-Ca-Cu-O system was demonstrated. Different laser excitation schemes for various metal elements are given in Table 1. It shows that commercially available lasers can be used to detect all desorbed neutral atoms and molecules. With an arrangement of multiple laser beams to do resonant excitation and ionization, several metal elements can be probed at the same time. Then, a real-time monitor for a superconductive thin film preparation can be achieved.

Table 1  
Resonance ionization schemes for various metal elements  
in metal oxide superconductors

					$\lambda$
Ba (6s <sup>2</sup> )	$\xrightarrow{h\nu}$	Ba (6s 7p)	$\xrightarrow{h\nu}$	Ba <sup>+</sup>	324.5 nm
Tl (6s <sup>2</sup> 6p)	$\xrightarrow{h\nu}$	Tl (6s <sup>2</sup> 7s)	$\xrightarrow{h\nu}$	Tl <sup>+</sup>	377.6 nm
Pb (6s <sup>2</sup> 6p <sup>2</sup> )	$\xrightarrow{h\nu}$	Pb (6s <sup>2</sup> 6p 7s)	$\xrightarrow{h\nu}$	Pb <sup>+</sup>	283.3 nm
Bi (6p <sup>3</sup> )	$\xrightarrow{h\nu}$	Bi (6p <sup>2</sup> 7s)	$\xrightarrow{h\nu}$	Bi <sup>+</sup>	306.8 nm
Ca (4s <sup>2</sup> )	$\xrightarrow{h\nu}$	Ca (4s 5p)	$\xrightarrow{h\nu}$	Ca <sup>+</sup>	273.6 nm
Y (4d 5s <sup>2</sup> )	$\xrightarrow{h\nu}$	Y (4d 5s 5p)	$\xrightarrow{h\nu}$	Y <sup>+</sup>	359.4 nm
Cu (3d <sup>10</sup> 4s)	$\xrightarrow{h\nu}$	Cu (3d <sup>10</sup> 4p)	$\xrightarrow{h\nu}$	Cu <sup>+</sup>	324.8 nm
Sr (5s <sup>2</sup> )	$\xrightarrow{h\nu}$	Sr (5s 6p)	$\xrightarrow{h\nu}$	Sr <sup>+</sup>	295.2 nm

It was observed that a large amount of  $O_2$  was desorbed during the laser ablation process. the amount of desorbed  $O_2$  was estimated as  $\sim 10^{10}$  molecules per pulse from laser ablation of a  $YBa_2Cu_3O_{7-x}$  target at 22°K with a very modest laser power density of  $1 \times 10^6$  W/cm<sup>2</sup>. With this laser power level, there should be no significant destruction of any chemical bonds. No significant numbers of atoms, molecules, or ions other than  $O_2$  were observed, as shown in Fig. 4(a). This process of desorption should be due to a heating effect. Since the desorption of  $O_2$  was observed for laser ablation by the fundamental Nd:YAG laser beam at 1064 nm, it is very unlikely the desorption was due to bond breaking of a metal oxide by the one-photon absorption process. The bond strength of Cu-O and Cu-O<sup>-</sup> were estimated by Sawyer<sup>22</sup> to be 2.8 and 3.1 eV, respectively. Thus, the present results indicated that  $O_2$  molecules were loosely trapped in these superconducting materials. Even a mild heating process is enough to drive out significant quantities of oxygen molecules trapped in these materials. The average velocity of desorbed  $O_2$  was estimated as  $\sim 7 \times 10^4$  cm/sec which indicated that the surface temperature was less than 300°C. There was a concern that the observed neutral  $O_2$  molecules could be due to the adsorption of  $O_2$  on the surface of the superconductor sample. To minimize this concern, a power density of  $1 \times 10^9$  W/cm<sup>2</sup> was used to vaporize the top layers of material for several minutes before making measurements of desorbed  $O_2$ . We also carefully checked to see that there was no  $H_2O$ ,  $N_2$ , or  $CO$  desorbed from the target to assure that the laser was probing below the original surface layer. These procedures rule out the possibility of  $O_2$  being adsorbed just on the surface. Therefore, the fact that oxygen molecules are trapped in  $YBa_2Cu_3O_{7-x}$  and Tl-Ca-Ba-Cu-O superconductors is confirmed.

It has been known for two decades that  $O_2$  can be trapped in an alkali-halide crystal.<sup>23</sup> Consequently, it should be much more likely that  $O_2$  can be trapped in loosely packed and very porous superconductor materials, which were produced and sintered either in air or in a pure oxygen environment. From our results, the existence of trapped  $O_2$  in the bulk of these superconductive materials is confirmed. The implication of trapped  $O_2$  inside of the bulk of superconductors can be quite significant. It has long been considered that the existence of  $Cu^{+3}$  accounts for the excess of oxygen in  $YBa_2Cu_3O_{7-x}$ . The nominal composition suggests that 33% of the copper is in the +3 state. However, no  $Cu^{+3}$  ions were observed by X-ray photoelectron spectroscopy. With the trapped molecular oxygen, there is no need to have  $Cu^{+3}$  account for the number of oxygen atoms to be higher than 6.5. This should have an important effect on the calculation of the electronic structure of these crystals. Since a very small isotope effect was observed for  $YBa_2Cu_3O_{7-x}$ , conventional BCS theory regarding electron-phonon coupling can not be used to account for this observation. However, if the trapped  $O_2$  molecule plays an important role in superconductivity, the isotopic effect can be expected to be much smaller if trapped  $O_2$  has only weak coupling to the crystal lattice. If the trapped  $O_2$  is critical for the superconductivity, the conservation of  $O_2$  in superconductive film becomes very critical for any practical application for these newly invented superconductors.

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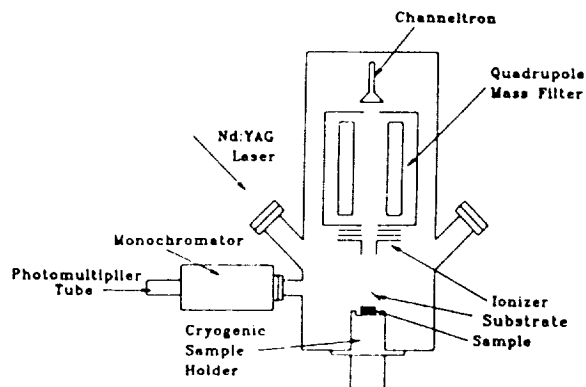


Fig. 1. Experimental schematic for fluorescence spectra, desorbed ion spectra, and resonance ionization spectra for laser ablation of the superconductors.

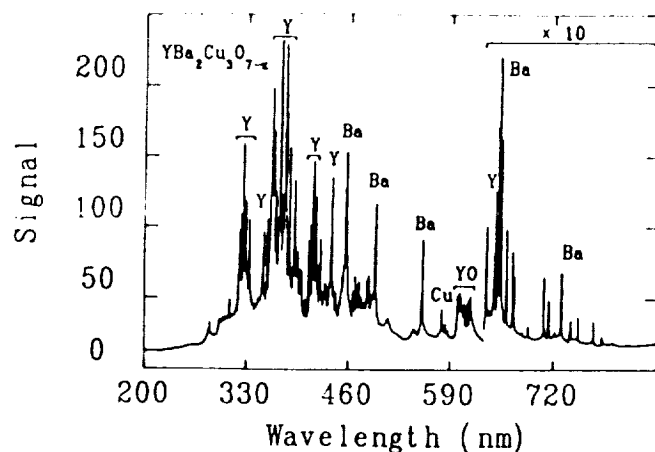


Fig. 2. Emission spectrum of laser ablation of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .

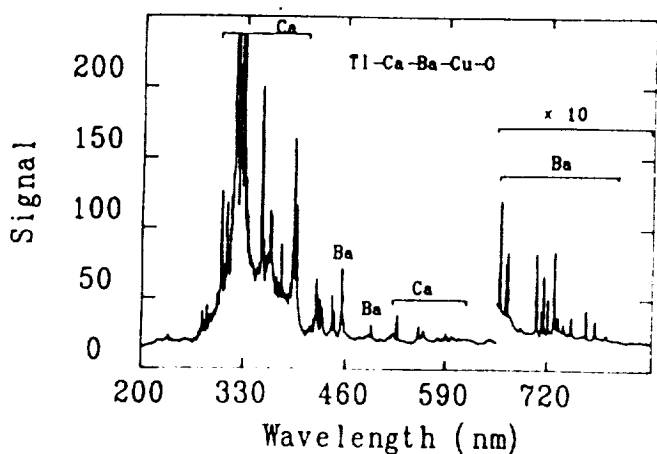


Fig. 3. Emission spectrum of laser ablation of  $\text{Tl-Ba-Ca-Cu-O}$  superconductors.

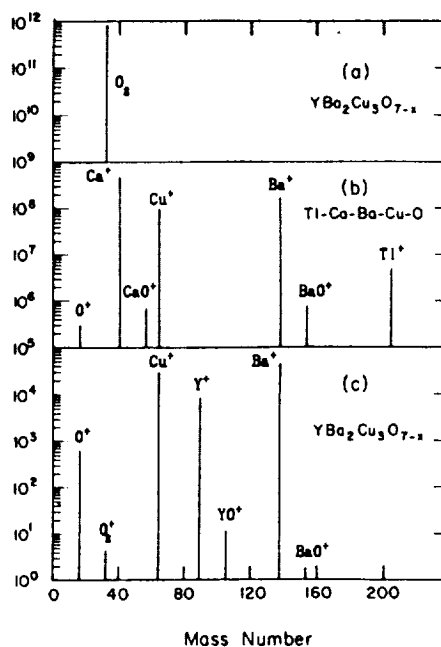


Fig. 4. Desorbed mass spectra from a laser ablation process of superconductor targets. (a) represents mass spectrum from  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  target with laser density at  $2 \times 10^6 \text{ W/cm}^2$ , the desorbed neutral  $\text{O}_2$  molecules were ionized by electron impact ionization. No other desorbed ions or molecules were observed. (b) and (c) represent desorbed ion spectra from  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and  $\text{Tl-Ba-Ca-Cu-O}$  targets, respectively. The ablation laser power density was  $2 \times 10^7 \text{ W/cm}^2$ . Filament was off.

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